Homogeneous nucleation of \(n\)-propanol, \(n\)-butanol, and \(n\)-pentanol in a supersonic nozzle

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We have measured the nucleation conditions of \(n\)-propanol, \(n\)-butanol, and \(n\)-pentanol in a supersonic Laval nozzle, and estimated that the maximum nucleation rate is \(5 \times 10^{10} \text{cm}^{-3} \text{s}^{-1}\) with an uncertainty factor of 2. Plotting the vapor pressures \(p_{\text{max}}\) and temperatures \(T_{\text{max}}\) corresponding to the maximum nucleation rate as \(\ln(p)\) versus \(1/T\), produces a series of well separated straight lines. When these values are scaled by their respective critical parameters, \(p_c\) and \(T_c\), the data lie close to a single straight line. Comparing the experimental data to the predictions of classical nucleation theory reveals much higher experimental rates, and the deviation increases with increasing alcohol chain length and decreasing temperature. A scaling analysis in terms of Hale’s scaled nucleation model [Phys. Rev. A 33, 4156 (1986); Metall. Trans. A 23, 1863 (1992)], clearly shows that our data are consistent with experimental nucleation rates measured using other devices that have characteristic rates many orders of magnitude lower. © 2005 American Institute of Physics. [DOI: 10.1063/1.1858438]

I. INTRODUCTION

Vapor phase condensation involves both nucleation and growth, and these processes can be better understood if many different experimental devices are employed to study the same chemical system. The difficulty is, however, to find substances and temperature ranges where all of the available devices can make accurate measurements.

The \(n\)-alcohols are one class of compounds whose nucleation and growth behavior has been studied using most of the available experimental techniques.\(^{1–11}\) This is because alcohols are easy to purify, have suitable vapor pressures and, importantly, condensation occurs above their respective triple points. Thus, all of the relevant thermophysical parameters including the equilibrium vapor pressure, surface tension, and density are accurately known. In 1995 \(n\)-pentanol was selected by the nucleation community as the best compound for a series of individual experiments on homogenous nucleation over as wide a range of nucleation rates as possible.\(^{11}\) The target temperature for which the nucleation rates should be measured by each technique was 260 K.

In our laboratory we measure nucleation rates in a supersonic Laval nozzle. The importance of this device to the joint experiments is that the characteristic nucleation rates in supersonic nozzles, \(J = 10^{16} - 10^{17} \text{cm}^{-3} \text{s}^{-1}\), are at least four to six orders of magnitude higher than any other experimental device. Thus, our results extend the isothermal nucleation rate measurements to much higher supersaturations and smaller critical cluster sizes. The combined data set provides a stringent test for both predictive nucleation rate equations and scaling laws.

In our gently diverging nozzles, we assume that the flow is one dimensional. In the absence of condensation the expansion is isentropic, and the pressure, density, and temperature all decrease monotonically. When the gas stream contains \(\sim 1\%\) of a condensible vapor, condensation can be induced in the supersonic section of the nozzle. The heat released by condensation then causes the state variables (e.g., pressure, density, temperature) to deviate from their isentropic values. The conditions corresponding to the onset of condensation in the nozzle are easily determined by comparing the condensing flow curve to the expected isentropic expansion (cf. Fig. 1). More quantitatively, the expansion history of the flowing gas can be determined by knowing the inlet conditions, measuring one state variable as a function of position along the nozzle, and determining the other flow properties by integrating the diabatic flow equations.\(^{12}\)

In our earlier work\(^{13–16}\) we developed techniques to determine the number density of the aerosol formed by condensation and the characteristic time interval over which nucleation occurred. Thus, we were able to make direct nucleation rate measurements in the supersonic nozzle. To date, we have...
measured homogeneous nucleation rates of H_2O, D_2O, and H_2O–D_2O mixtures in supersonic nozzles and found that they are consistent with results available in the literature at much lower supersaturations.\textsuperscript{3,15} In the present work we examine the nucleation behavior of three n-alcohols; n-propanol, n-butanol, and n-pentanol. From static pressure measurements we determine the conditions at the onset of condensation, as well as the characteristic time interval \( \Delta t_{\text{max}} \) temperature \( T_{\text{max}} \), and supersaturation \( S_{\text{max}} \) or condensible pressure \( p_{\text{max}} \) corresponding to the maximum nucleation rate. Based on our previous experiments with water nucleation in the same nozzle, we estimate the number density of the aerosol, and, thus, determine the peak nucleation rates as a function of \( S_{\text{max}} \) and \( T_{\text{max}} \). We compare our estimated nucleation rates for n-pentanol to the rate measurements available in the literature and to the predictions of classical nucleation theory (CNT). Finally, for each of the n-alcohols, we use Hale’s scaling formalism\textsuperscript{17,18} to compare our estimated nucleation rates to those reported in the literature, and to extract estimates for the empirical scaling constant \( \Omega \) for each substance. For water, Hale recently showed that the scaling formalism is a powerful way to detect inconsistencies between different experimental data sets.\textsuperscript{19}

II. EXPERIMENT

A. Chemicals

The condensible materials studied were n-propanol (99.5%, Sigma-Aldrich Co., St. Louis, MO), n-butanol (99.8%, Sigma-Aldrich Co.), and n-pentanol (99%+, Alfa Aesar, Karlsruhe, Germany). The n-pentanol is from the same lot used by other members of the joint nucleation experiment. The alcohols were not purified further. The carrier gas was nitrogen. The thermophysical properties of the chemicals are summarized in Table I.

B. Nozzle flow apparatus

The apparatus, illustrated in Fig. 2, is identical to that used by Kim \textit{et al.}\textsuperscript{15} except for the additional in-line electric heater required for the high temperature \((T_0=50 - 60 \, ^\circ\text{C})\) experiments. The system works as follows. Nitrogen is drawn from the gas side of two 230 L liquid N_2 cylinders that are placed on balances in order to measure the N_2 consumption rate. Electrical heaters warm the gas leaving the cylinders. The main N_2 stream flows through a ballast tank, a filter, and the additional in-line heater. The second N_2 stream is split, heated further, and enters the vaporizer where part of the flow disperses the condensible liquid into a fine spray while the remainder provides the energy to evaporate the droplets and dilutes the vapor. The condensible under study (a liquid at room temperature and pressure) is pumped from a flask into the vaporizer using a peristaltic pump. The mass flow rate of the liquid is determined by monitoring the weight change of the flask as a function of time. The vapor rich gas stream combines with the main N_2 gas and the mixture flows through a heat exchanger placed in a temperature controlled circulating water bath. This thermostat also controls the temperature in the plenum, while the plenum pressure is controlled by adjusting the N_2 flow rate. The plenum and nozzle are located in a large metal box with a lid to reduce heat transfer to the environment.

The temperature of the mixture leaving the plenum is measured using a platinum resistance temperature detector (RTD) located in the center of a short flow straightener. Finally the gas mixture flows through the Laval nozzle where a movable pressure probe measures the static pressure of the flow as a function of axial position along the centerline of the nozzle. The flow is pumped to atmospheric pressure using two rotary vane vacuum pumps.

All of the experiments in this study used our standard nozzle-nozzle A.\textsuperscript{14,15} The cross-sectional area of the throat \( A' \), based on the flow rate of N_2 through the nozzle, is 59.1 mm\(^2\) and the expansion rate, based on measuring the effective area ratio, is \( d(A/A')/dx=0.048 \, \text{cm}^{-1} \).

C. Pressure trace experiments

Our supersonic Laval nozzles are designed so that the flow can be treated as one dimensional, and, thus, the entire history of the expansion can be obtained by measuring the initial, or stagnation, conditions and one state variable as a function of position along the nozzle. Here, we measure the static pressure along the length of the nozzle using a movable static pressure probe for both pure N_2 and for the condensing vapor mixtures. In the absence of condensation, the isentropic relationships hold and we can directly determine the effective area ratio of the nozzle. To derive the properties of the condensing flow (local gas velocity \( u \), temperature \( T \), density \( \rho \), condensate mass fraction \( g \)), we integrate the diabatic flow equations using the pressure and area ratio as the known quantities.\textsuperscript{12}

The vapor pressure of the condensable \( p_v(x) \) is related to the initial conditions and the condensate mass fraction by
TABLE I. The thermophysical properties of n-propanol, n-butanol, and n-pentanol. The properties are \( \mu \), the molecular weight; \( C_p^l \), heat capacity of the liquid; \( C_p^v \), heat capacity of the vapor at constant pressure; \( p^\sigma \), equilibrium vapor pressure (Ref. 26); \( T \), temperature in Kelvin; \( \rho_l \), liquid density (Ref. 27); \( \sigma \), surface tension (Ref. 28); \( \Delta H_{vap} \), heat of vaporization; and \( R \), universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

<table>
<thead>
<tr>
<th></th>
<th>n-propanol</th>
<th>n-butanol</th>
<th>n-pentanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu ) (g mol(^{-1}))</td>
<td>60.10</td>
<td>74.12</td>
<td>88.15</td>
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<td>( T_c ) (K)</td>
<td>536.4</td>
<td>563.1</td>
<td>588.2</td>
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<tr>
<td>( C_p^l ) (at 298.15 K) (J g(^{-1}) K(^{-1}))</td>
<td>2.3910</td>
<td>2.3880</td>
<td>2.3607</td>
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<tr>
<td>( C_p^v ) (at 298.15 K) (J g(^{-1}) K(^{-1}))</td>
<td>1.4243</td>
<td>1.6541</td>
<td>1.5099</td>
</tr>
<tr>
<td>( p^\sigma ) (Pa)</td>
<td>( \exp(150.248 - 11286.5/T - 19.19 \times \ln T) \times 133.322 )</td>
<td>( \exp(106.705 - 9956.06/T - 12.52 \times \ln T) \times 133.322 )</td>
<td>( \exp(138.313 - 11785.47/T - 17.19 \times \ln T) \times 133.322 )</td>
</tr>
</tbody>
</table>
| \( \rho_l \) (kg m\(^{-3}\)) | 1.01077 \times 10\(^3\) - 3.99649 \times 10\(^3\) \times T - 6.64923 \times 10\(^3\) 
\( \times T^2 \) 
\( + 2.16751 \times 10\(^5\) \times T - 2.46167 \times 10\(^4\) \times T^4 \) | 1.15309 \times 10\(^3\) - 2.13457 \times T + 5.15573 \times 10\(^3\) \times T^2 
\( - 6.38112 \times 10\(^4\) \times T^3 \) | 1.0033 \times 10\(^3\) - 1.58026 \times T + 3.34384 \times 10\(^3\) \times T^2 
\( - 4.34342 \times 10\(^4\) \times T^3 \) |
| \( \sigma \) (N m\(^{-1}\)) | 25.28 \times 10\(^{-3}\) - 8.394 \times 10\(^{-3}\) \times (T - 273.15) | 25.98 \times 10\(^{-3}\) - 8.181 \times 10\(^{-3}\) \times (T - 273.15) | 26.78 \times 10\(^{-3}\) - 8.147 \times 10\(^{-3}\) \times (T - 273.15) |
| \( \Delta H_{vap} \) (J mol\(^{-1}\)) | \( R \times (8559.61 - 9.29 \times T) \) | \( R \times (9412.61 - 10.54 \times T) \) | \( R \times (9788.38 - 9.90 \times T) \) |

D. Determining \( \rho_J^{max}, T_J^{max} \) and \( \Delta t_J^{max} \)

To determine the parameters corresponding to the peak nucleation rate for each condensation experiment, we calculate the nucleation rate as a function of position using the experimentally derived temperature and supersaturation profiles and the classical nucleation rate expression derived by Becker and Döring.\(^20\) Thus, the nucleation rate \( J_{BD} \) is given by

\[
J_{BD} = \sqrt{\frac{2 \sigma}{\pi \rho_{v,m} v_m} \left( \frac{p_v}{kT} \right)^2 \exp \left( \frac{-16 \pi v_{m}^{2} \sigma^{3}}{3(kT)^{3} (\ln S)^{2}} \right)},
\]

where \( \sigma \) is the surface tension of the macroscopic fluid-vapor interface, \( v_m \) is the molecular volume, and \( k \) is the Boltzmann constant. From the nucleation rate profile in the nozzle it is easy to determine the values of \( S \) and \( T \) that correspond to the maximum nucleation rate, and hence determine the corresponding pressure of the condensable vapor, \( p_J^{max} \).

As discussed in detail in our earlier work,\(^14,15\) the characteristic time corresponding to \( J_{max} \) and \( \Delta t_J^{max} \) is given by

\[
\Delta t_J^{max} = \frac{1}{J_{max} \rho_J^{max}} \int_{S_{max}}^{S_{0}} \tau_{BD},
\]

where \( \tau_{BD} \) is the characteristic time corresponding to the equilibrium vapor pressure of the condensable species.
where \( V_{NZ} \) is the volumetric flow rate in the nucleation zone, \( V_{NZ} = (\dot{m}_i + \dot{m}_e) / \rho_{NZ} = \dot{m}_i / \rho_{NZ} \), and \( \rho_{NZ} \) is the density of the gas in the nucleation zone.

III. RESULTS AND DISCUSSION

A. Pressure trace experiment

The stagnation pressure \( p_0 \) for all of the experiments was 59.6±0.02 kPa, while the stagnation temperatures \( T_0 \) were varied between 35 and 60 °C to compensate for the differences in vapor pressure of the \( n \)-alcohols. As illustrated in Fig. 1, condensation introduces a deviation of the pressure trace from the dry adiabatic expansion. As the amount of condensible decreases, the onset of condensation moves downstream to lower temperature and the deviation from the isentrope decreases. Table II summarizes the experimental conditions and the results for the current \( n \)-alcohol measurements. In our work, we define the onset of condensation to be the point at which the temperature of the condensing flow curve is 0.5 K higher than that of the isentropic expansion of the same gas mixture through the same nozzle. We note that the agreement between the current onset data and that measured earlier in our lab\(^{21} \) is very good.

Although the onset of condensation is a convenient parameter to characterize the limit of stability in an expanding flow, the definition of this term depends on the experimental device used. Furthermore, in a nozzle this parameter depends both on nucleation and droplet growth. In nucleation studies, it is more important to determine the pressure \( p_{J_{\text{max}}} \) and temperature \( T_{J_{\text{max}}} \) that correspond to the maximum nucleation rate. As discussed in an earlier paper,\(^{15} \) the results of the calculations outlined in Sec. II D are insensitive to the particular nucleation rate expression chosen. This is because most reasonable nucleation theories properly predict the supersaturation dependence of experimental nucleation rate data and have roughly the same temperature dependence over the 1–5 K temperature change that occurs near the supersaturation peak in our experiments. The \( p_{J_{\text{max}}}, T_{J_{\text{max}}} \) values derived from the experiments are summarized in Table II, and plotted in Fig. 3(a). As discussed by Volmer\(^{22} \) as early as 1939, lines of constant nucleation rate should be straight lines in a \( \ln p \) versus \( 1/T \) plot, and over the ~40 K temperature range investigated here our data clearly follow this trend. The data in Fig. 3(a) also exhibit a systematic behavior for this homologous series of alcohols. We therefore reduced the pressures by the critical pressure \( p_c \) and the temperatures by the critical temperature \( T_c \) using the recent data of Gude and Teja.\(^{23} \) As illustrated in Fig. 3(b), the three curves now lie close to a single line suggesting that the nucleation behavior should be discussed in terms of a scaled nucleation theory. We will perform such analysis towards the end of this paper.
### Table II. The results of pressure trace experiments for n-propanol, n-butanol, and n-pentanol. The stagnation pressure $p_s$ is fixed at 59.6 kPa, $m$ is the mass flow rate, $\gamma$ is the initial mole fraction of the condensible, $T_s$ is the stagnation temperature, $p_{on}$ and $T_{on}$ are the onset pressure and temperature, and $p_{max}$, $T_{max}$, and $S_{max}$ are the pressure, temperature, and supersaturation corresponding to the maximum nucleation rate $J_{max}$ respectively.

<table>
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<tr>
<th>$m$ (g min$^{-1}$)</th>
<th>$\gamma$</th>
<th>$T_s$ (K)</th>
<th>$p_{on}$ (kPa)</th>
<th>$T_{on}$ (K)</th>
<th>$p_{max}$ (kPa)</th>
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<td>0.038</td>
<td>236.39</td>
<td>66</td>
</tr>
</tbody>
</table>

### B. Nucleation rate estimates

To properly determine the nucleation rate,\textsuperscript{14,15} we need both the characteristic time associated with the peak nucleation rate $\Delta t_{max}$ and the number density $N$ of the aerosol. The peak nucleation rate is then given by

$$ J = N \frac{\rho_{NZ}}{\Delta t_{max} \rho_{NV}}, $$

where the ratio $\rho_{NZ}/\rho_{NV}$ accounts for the change in gas density between the region where the particles were formed—the nucleation zone—and the region where the number density was measured—the viewing volume.

From the pressure trace measurements we found that in the current work $\Delta t_{max}$ varied by less than a factor of 2 and was always in the range $6.2 \times 10^{-5} < \Delta t_{max} / s < 1.1 \times 10^{-5}$. These values are quite close to those found in our earlier work on D$_2$O nucleation in the same nozzle where $9 \times 10^{-6} < \Delta t_{max} / s < 1.6 \times 10^{-5}$. For our D$_2$O and H$_2$O nucleation rate measurements we were able to use small angle neutron scattering experiments to accurately characterize the aerosol. Unfortunately, the scattering length density of the alcohols (C$_n$H$_{2n+1}$OH) is even closer to zero than that of H$_2$O, making quantitative scattering measurements extremely difficult. Furthermore, the cost of deuterated alcohols (C$_n$D$_{2n+1}$OD) is 10–100 times the cost of D$_2$O and, thus, neutron scattering experiments were not deemed feasible for this study.

We instead relied on the observation that for all of the H$_2$O and D$_2$O experiments conducted with nozzle A, the number density was always between $5 \times 10^{11} < N / \text{cm}^{-3} < 1 \times 10^{12}$. These values are in good agreement with those estimated by Wegener, Clumpner, and Wu\textsuperscript{24} based on light scattering measurements from water droplets in a very simi-
lar supersonic nozzle under comparable operating conditions. Furthermore, in light scattering experiments from ethanol droplets, again formed in a similar nozzle, Clumpner also estimated that the aerosol number densities were between \(10^{11}, N/cm^3\), \(10^{12}\) for comparable partial pressures of the condensable. We therefore believe that the number density of the \(n\)-alcohol aerosols formed in our nozzles most likely lie in the range \(10^{11}, N/cm^3\), \(10^{12}\).

In the D\(_2\)O nucleation rate experiments we found that the aerosol number density increased systematically with \(D_{TJ}^{\text{max}}\). Combining this observation with our estimates for \(N\) and \(D_{TJ}^{\text{max}}\), we determined that reasonable upper and lower bounds on the nucleation rates for the \(n\)-alcohols are \(2 \times 10^{16} < J/cm^3 s^{-1} < 1 \times 10^{17}\). Finally, we note that in D\(_2\)O experiments conducted with nozzle A the peak nucleation rate was essentially independent of the operating conditions. We therefore assumed that this also holds for the \(n\)-alcohols, and assigned a single characteristic peak nucleation rate to all of the experiments of \(J = 5 \times 10^{16} cm^3 s^{-1}\) with a factor of uncertainty equal to \(\sim 2\).

C. Critical supersaturation values and a comparison with classical nucleation theory (CNT)

Figure 4 illustrates the comparison between the experimental measurements and the predictions of classical nucleation theory (CNT) corresponding to a nucleation rate of \(J = 5 \times 10^{16} cm^3 s^{-1}\). As expected, the data and the theoretical calculations exhibit the same trend—the critical supersaturation increases as the temperature decreases. CNT, however, overestimates the critical supersaturation over the entire temperature range, and this deviation increases both with decreasing \(T\) and increasing alcohol chain length. Furthermore, the spacing between the predicted \(S-T\) curves for the three alcohols is relatively constant, while the spacing between the \(n\)-butanol and \(n\)-propanol data is distinctly smaller than the spacing between the \(n\)-butanol and \(n\)-pentanol data.

D. \(n\)-pentanol nucleation rates and comparison with previous results

Of the three alcohols studied here, the most extensive rate data set is that for \(n\)-pentanol. Figure 5 summarizes the available data by comparing the values of \(p_{J^{\text{max}}}\) and \(1/T_{J^{\text{max}}}\) measured in this study with the measurements available in the literature. The solid line is the fit to the nozzle data that we used to extrapolate our results to both 250 K and the target temperature of 260 K. At a fixed temperature our values of \(p_{J^{\text{max}}}\) lie above the other data because the characteristic nucleation rate for nozzles is four to six orders of magnitude higher than those of other devices. This trend is nicely
demonstrated in the range from 240 to 260 K where the data from nucleation pulse chambers \((J=10^3 \text{ cm}^3 \text{ s}^{-1})\), expansion wave tubes \((J=10^{10} \text{ cm}^3 \text{ s}^{-1})\) and supersonic nozzles \((J=5 \times 10^{16})\) are cleanly separated. At 260 K, the trend from the lowest characteristic nucleation rate (thermal diffusion cloud chamber) to highest characteristic nucleation rate (extrapolated supersonic nozzle data) is also well preserved. As the temperature increases, however, the distinction between the different techniques becomes more difficult to discern. In particular the slope of the thermal diffusion cloud chamber data, chamber I\(^7\), does not seem consistent with the results of the other experimental techniques.

We then compared our estimated nucleation rates with the measurements available in the literature at \(T=250\) K, Fig. 6, and 260 K, Fig. 7. In each of these figures, the dashed line is the prediction of CNT, while the solid line is the prediction of CNT multiplied by a constant factor. In both figures our estimates of the nucleation rate line up well with the measurements from the literature at both temperatures. Furthermore, once CNT is suitably adjusted, the rates agree quantitatively with the measurements over 17 orders of magnitude.

**E. Comparison with Hale’s scaling theory**

Hale’s scaling formalism\(^{17-19}\) suggests replacing the temperature dependent parameters in Eq. (4) by scaling laws expressed in \(\varepsilon\), the distance from the critical point \(\varepsilon=(T_c−T)/T_c\), where \(T_c\) is the critical temperature. She introduced \(\sigma=\sigma_0\varepsilon^\alpha\) for the surface tension and \(\rho_1−\rho_0=\rho_0\varepsilon^\beta\) for the density where \(\sigma_0\) and \(\rho_0\) are the critical amplitudes, and \(\mu\) and \(\beta\) are the critical exponents. For the three-dimensional Ising model, the universality class to which our vapor systems belong, \(\mu=1.26\) and \(\beta=0.32\). After a number of simplifying assumptions \((\rho_1 \gg \rho_0, 3\mu-2\beta \sim 3, v_m=\mu_0/\rho_1)\) Hale arrived at a scaled model with the following nucleation rate expression.
\[ J_{\text{scaled}} = J_0 \exp \left( \frac{16\pi}{3} \Omega \left[ \frac{T_c}{T} - 1 \right] \frac{1}{(\ln S)^2} \right), \]  

(7)

where \( J_0 \), the kinetic prefactor, is assumed to be given by one event per second and thermal wavelength (evaluated at the critical point) cubed, and was eventually set equal to \( J_0 = 10^{26} \text{ cm}^{-3} \text{ s}^{-1} \). The parameter \( \Omega \) is given by

\[ \Omega^3 = \frac{\sigma_m^2 \mu_m^2}{p_0^2 k T_c^3}, \]

(8)

where \( \mu_m \) is molecular mass. Physically, \( \Omega \) can be thought of as the surface entropy per molecule (divided by \( k \)), and is calculated from the constants found by fitting the bulk physical properties of the condensible material.\(^{18}\)

As noted first by Binder and Stauffer,\(^{19}\) the virtue of the parameter \( C_0 (T_c/T - 1)^3/(\ln S)^2 \) is that it simultaneously accounts for the temperature and supersaturation dependence in the exponent of the nucleation rate expression, Eq. (7). Hale’s model, therefore, provides a basis to compare experimental nucleation rates of any magnitude measured at arbitrary temperature and supersaturation. A plot of the data as \(-\ln(J/10^{26})\) versus the parameter \( C_0 (T_c/T - 1)^3/(\ln S)^2 \) yields a straight line, and by adjusting \( C_0 \) until the data conform to the straight line with a slope equal to 1, the effective value of \( \Omega \) can be derived from \( C_0 \) by

\[ \Omega = \left( \frac{3C_0}{16 \pi} \times \ln 10 \right)^{1/3}. \]

(9)

Figure 8 uses this formalism to compare our estimated nucleation rates for \( n \)-propanol, \( n \)-butanol, and \( n \)-pentanol to the measurements available in the literature. The supersonic nozzle data are represented by a horizontal line that spans the extremes of our measurement range. A vertical error bar represents the estimated uncertainty of the nucleation rate. Other literature data are plotted as symbols. The estimated values of \( C_0 \) are noted on the graph as are the effective values of \( \Omega \). We did not attempt to optimize the value of \( C_0 \) by a weighted least squares fit because it is not clear how to properly weight the different data sets. Plotting the data this way clearly demonstrates that almost all of the measured nucleation rates for the \( n \)-alcohols scale well. The scatter in our data, in terms of the scaled supersaturation, is similar to that of the other measurements. Because we have assigned a constant nucleation rate to our results there is no change in the scaled nucleation rate. The only data that seem to deviate significantly from the scaling law are the \( n \)-pentanol nucleation rate measurements made using a thermal diffusion cloud chamber.\(^{7}\) The data point corresponding to 260 K is closest to the straight line and the disagreement increases as the temperature is raised. Hale claims her model should work best when \( T/T_c < 0.5 \). Given that \( T_c \) for \( n \)-pentanol is 588 K, this may explain part of the deviation observed at high temperature for this data set.

In theory, the value of \( \Omega \) depends on the degree of the association of the liquid. Hale has found a value of about 2.1 for simple liquids and 1.5 for associated liquids.\(^{18}\) As the chain length of an \( n \)-alcohol increases, the degree of association decreases, and the value of \( \Omega \) is expected to increase.
This prediction is in agreement with the experimental values of \( \Omega \) found in this study for these three alcohols: \( \Omega_{n\text{-propanol}} = 1.76 \), \( \Omega_{n\text{-butanol}} = 1.84 \), \( \Omega_{n\text{-pentanol}} = 1.90 \). Finally, the experimental values of \( \Omega \) are \( \sim 10\% – 25\% \) higher than those derived from fits \(^{10} \) to the physical property data where: \( \Omega_{n\text{-propanol}} = 1.43 \), \( \Omega_{n\text{-butanol}} = 1.57 \), \( \Omega_{n\text{-pentanol}} = 1.71 \).

IV. CONCLUSIONS

We examined the condensation of \( n\text{-propanol} \), \( n\text{-butanol} \), and \( n\text{-pentanol} \) in our standard supersonic nozzle. The pressures and temperatures at the onset of condensation were determined from axial pressure measurements in the nozzle and are in very good agreement with those measured earlier by Dieregsweiler.\(^{21} \)

We then determined the pressures and supersaturations that correspond to the maximum nucleation rate over a 40 K temperature range, and found that the pressures increase exponentially with temperature and decreasing chain length, while the supersaturations increase with decreasing temperature and increasing chain length. The dependence of the critical supersaturation \( S_{\text{crit}} \)-temperature \( T \) data are in qualitative agreement with CNT predictions, however, the theory consistently overestimated the critical supersaturation values. While the spacing between the \( S_{\text{crit}} - T \) curves of \( n\text{-pentanol} \) and \( n\text{-butanol} \) from the data was consistent with the predictions of CNT, the spacing between the \( n\text{-butanol} \) and \( n\text{-propanol} \) curves is smaller for the data than for the theory.

The peak nucleation rate was estimated to be \( J = 5 \times 10^{16} \text{ cm}^{-3} \text{ s}^{-1} \) with an error range equal to \( 2 \times 10^{16} < J/\text{cm}^{-3} \text{ s}^{-1} < 1 \times 10^{17} \). We reiterate that the value of the aerosol number density used to calculate \( J \) was not measured directly, but was estimated based on analogy with extensive \( D_2O \) small-angle neutron scattering measurements. The peak rates were directly compared to the predictions of CNT and other experimental measurements found in the literature for \( n\text{-pentanol} \) at \( T = 250 \) and 260 K and the agreement was very good. Hale’s scaling theory was used to compare the estimated rates for each species over a wider range of temperature and supersaturation and all of the data scale rather well.

These results are extremely encouraging and emphasize the importance of additional SANS experiments to measure the aerosol number density directly in order to verify our estimates. Current efforts in this direction are in progress in our laboratory.

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\(^{30}\)These values were derived by fitting a straight line to a plot of \( \Omega r/(\rho_0^{2/3} kT) \) vs \( 1/T \) and setting \( \Omega \) to the slope divided by \( T_r \). Here \( \rho_0 \) is the liquid number density [B. Hale (private communication)].